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Photocatalytic degradation of Metronidazole with illuminated TiO₂ nanoparticles

Mahdi Farzadkia¹, Edris Bazrafshan², Ali Esrafil¹, Jae-Kyu Yang³ and Mehdi Shirzad-Siboni^{1*}

Abstract

Metronidazole (MNZ) is a brand of nitroimidazole antibiotic, which is generally used in clinical applications and extensively used for the treatment of infectious diseases caused by anaerobic bacteria and protozoans. The aim of this investigation was to degrade MNZ with illuminated TiO₂ nanoparticles at different catalyst dosage, contact time, pH, initial MNZ concentration and lamp intensity. Maximum removal of MNZ was observed at near neutral pH. Removal efficiency was decreased by increasing dosage and initial MNZ concentration. The reaction rate constant (k_{obs}) was decreased from 0.0513 to 0.0072 min⁻¹ and the value of electrical energy per order (E_{EO}) was increased from 93.57 to 666.67 (kWh/m³) with increasing initial MNZ concentration from 40 to 120 mg/L, respectively. The biodegradability estimated from the BOD5/COD ratio was increased from 0 to 0.098. The photocatalyst demonstrated proper photocatalytic activity even after five successive cycles. Finally, UV/TiO₂ is identified as a promising technique for the removal of antibiotic with high efficiency in a relatively short reaction time.

Keywords: Titanium dioxide, Metronidazole, Photocatalysis, Kinetics

Background

Recently, several different types of emerging contaminants in water systems are known as new environmental hazards those need to be treated with suitable methods [1]. As various pharmaceutical compounds have been used since the 1950s due to rapid population growth and development of medical science, several pharmaceutical compounds have been found in surface water, ground water and effluents from wastewater treatment plants. Metronidazole (2-methyl-5-nitroimidazole-1-ethanol) has been widely used to treat infections caused by anaerobic bacteria, bacteroides and protozoa [2-4]. Residual concentrations of metronidazole (MNZ) in surface waters and wastewater are 1 ~ 10 ng/L [5,6]. As MNZ is non-biodegradable and highly soluble in water, it can be accumulated in the aquatic environment [7,8]. Elimination of MNZ from water system is an important issue considering its toxicity, potential mutagenicity and carcinogenicity [7,8]. In order to remove MNZ, many techniques such as adsorption [9,10], reduction with nanoscale zero-valent iron particles [11], biological methods [12,13],

ozonation technology [14], photolysis [15], Fenton and photo-Fenton processes [16], heterogeneous photocatalysis [15,17,18] and electro-Fenton process with a Ce/SnO₂-Sb coated titanium anode [1] have been applied.

Adsorption is widely used method for the treatment of wastewater containing toxic organic compounds. However, it just transfer contaminants from water to a solid phase without any degradation [9,10,19,20]. Biological method is also known as one of the suggested techniques. However this method generally requires long periods for treatment [12,21]. Oxidation is a promising process but sometimes it is regarded as a limited process due to the formation of intermediates with higher toxicity than the parent compound [5,8,22]. Therefore near complete mineralization of MNZ is the most relevant option. For this purpose, advanced oxidation process (AOP) is regarded as a promising option to treat wastewater containing MNZ due to a complete mineralization of parent material as well as lack of selectivity [7,23]. Generally AOPs involve generation of hydroxyl radicals through UV/photocatalyst, UV/H₂O₂ and UV/O₃ processes [24-26]. Among these methods, photocatalytic reaction using TiO₂/UV can treat non-biodegradable organic compounds to biodegradable species [23,24,27]. Considering characteristics of the AOP, it can be used as pre- or post-

* Correspondence: mshirzadsiboni@yahoo.com

¹Department of Environmental Health Engineering, School of public Health, Iran University of Medical Sciences, Tehran, Iran

Full list of author information is available at the end of the article

treatment process in wastewater treatment because of its installation easiness in conventional wastewater treatment facilities [23,24,27].

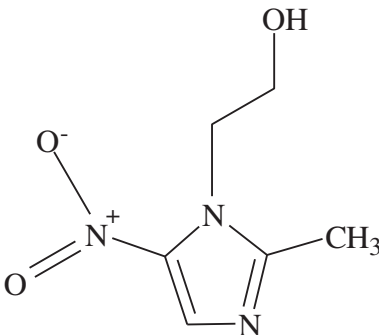
Therefore, in the present work, P-25 TiO₂ was selected as a catalyst in the photocatalytic removal of MNZ. Effects of several operational parameters including pH, TiO₂ dosage and MNZ concentration on photocatalytic degradation of MNZ were investigated. Kinetic parameters for the photocatalytic degradation were obtained by application of the Langmuir–Hinshelwood (L–H) model. Finally, electrical energy per order (E_{EO}) was obtained to evaluate cost-efficiency of the processes used in this research.

Material and methods

Chemicals

Analytical grade of MNZ (C₆H₉N₃O₃; 99% chemical reagent) was purchased from Merck (Darmstadt, Germany) and its physical and chemical characteristics are summarized in Table 1. Potassium dihydrogen phosphate (KH₂PO₄) and acetonitrile (99.7%, HPLC grade) were purchased from Merck. P-25 TiO₂ (80/20 mixture of anatase and rutile) was obtained from Degussa Corp. It has approximately spherical shape and has greater than 99.5% purity. The specific surface area of the TiO₂ particles was 50 ± 15 m²/g according to Evonik-Industrial Co. The average size of the TiO₂ particles was 21 nm.

Table 1 Physical and chemical properties of MNZ

Characteristic	Metronidazole antibiotic (MNZ)
Molecular structure	
Molecular formula	C ₆ H ₉ N ₃ O ₃
Molecular weight (g/mol)	171.2
Water solubility (g/L)	9.5
pK _a	2.55
Melting point (°C)	159–163
K _H (mol/dm ³ .atm)	5.92 × 10 ⁷
V _p (Pa)	4.07 × 10 ^{−7}

The antibiotic aqueous solution was prepared by dissolving 1 g of MNZ in 1 L distilled water. The antibiotic aqueous solution was prepared weekly and stored at 4°C. Initial COD and BOD₅/COD ratio of 1000 mg/L MNZ was 126 mg/L and approximately 0, respectively.

Figure 1a and b shows X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR) image of TiO₂, respectively. The main peaks at 2θ values of 25.367, 37.909, 38.667, 48.158, 54.051, 55.204, 62.817 and 68.976 were correspond to the (101), (004), (112), (200), (105), (211), (204) and (116) planes of P-25 TiO₂ (JCPDS card no. 36–1451). FT-IR analysis of TiO₂ was performed in the range of 400–4000 1/cm (Figure 1b). The absorption bands at 438 1/cm and 620 1/cm was attributed to the E_g and A_{2g} mode, respectively. The pH_{ZPC} of TiO₂ nanocatalyst was determined adopting the previously reported method.

Experimental set-up

The experimental reactor used for the photocatalytic degradation of MNZ is shown in Figure 2. The total volume of the reactor was 2 L with working volume of 1 L. The solution in the reactor was constantly stirred via a magnetic stirrer (170 rpm). A 125 W medium-pressure UVC lamp emitting maximum wavelength at 247.3 nm and a low-pressure UV lamp with irradiation intensity 8 W were applied as light sources. The light intensity of the UVC lamp was equal to 1020 μW/cm² measured by a Spectroline model DRC-100X digital radiometer combined with a DIX-365 radiation sensor (ShokofanTosee, Company, Iran).

Experimental procedure and analysis

In batch experiments, a selected dosage of TiO₂ (0.5–3 g/L) was added in 1000 mL of MNZ solution with a certain concentration (40–120 mg/L) at different solution pH ranging from 3 to 11. Initial pH of the solution was adjusted by adding NaOH and HCl (0.1 mol/L) and measured by pH meter (Metron, Switzerland). All runs were performed under ambient conditions for 3 h. During the experiments, the solution in the photoreactor was constantly stirred and kept at constant temperature (25 ± 1°C). The MNZ solutions loaded with TiO₂ were equilibrated in the dark for 30 min. After the equilibration period, the UV-lamp was switched on and 10 mL of the solution was taken at distinct time intervals. The aqueous samples were centrifuged (Sigma-301, Germany) at 4000 revolution per minute (rpm) for 10 min to eliminate TiO₂ and then measured concentration of residual MNZ. The concentration of residual MNZ was determined by high performance liquid chromatography (HPLC, Waters, USA) equipped with a UV detector at 348 nm. A Diamonsil (R) C18 column (5 μm, 250 mm long × 4.6 mm ID) was used. The data were recorded by a chemistation software.

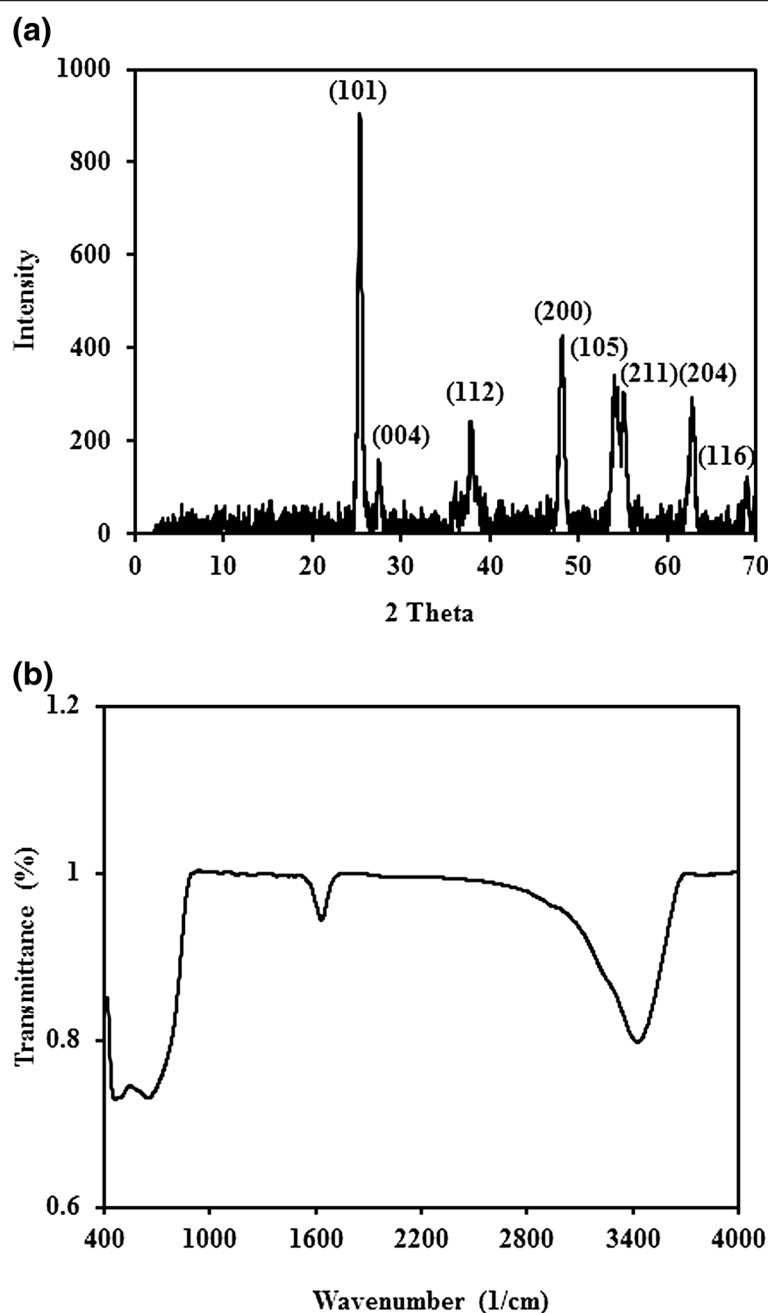


Figure 1 Characteristics of titanium dioxide: (a) XRD pattern (b) FT-IR pattern.

The mobile phase was composed of a mixture of acetonitrile and distilled water (30/70, v/v). The flow speed was set at 1.0 mL/min and 20 μ L injections were used [4]. COD was determined by COD reactor model AR851 (HACH, USA) and biodegradability was measured by five-day biochemical oxygen demand (BOD5) according to the Standard Methods [28]. A typical HPLC chromatogram of MNZ is shown in Figure 3.

The removal efficiency (%) is calculated by Eq. (1).

$$\text{Removal efficiency (\%)} = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

where C_0 and C are the concentrations of MNZ at initial and at time t (mg/L), respectively.

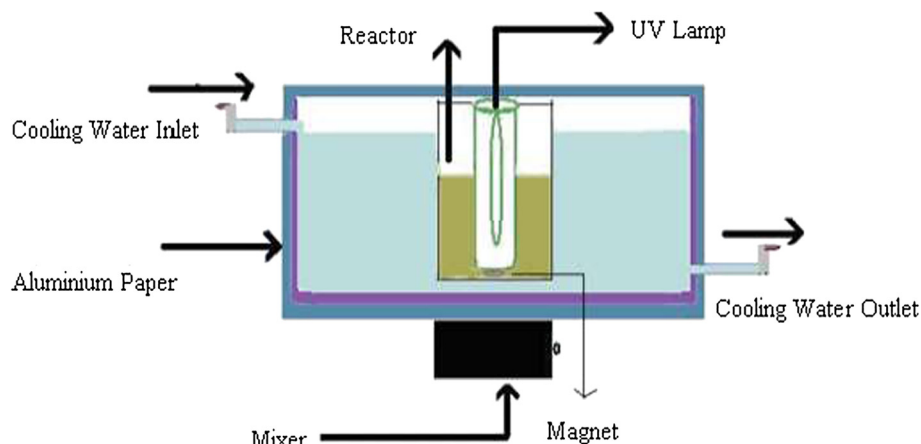


Figure 2 A schematic diagram of the experimental reactor.

All experiments were repeated three times and the average values with error percents were reported.

Results and discussion

Effect of TiO_2 dosage

Effect of TiO_2 dosage on the photocatalytic degradation of MNZ (80 mg/L) was investigated at pH 7. As shown in Figure 4, degradation efficiency of MNZ was increased from 64.28 to 97.61% by increasing irradiation time from 30 to 180 min at 0.5 g/L TiO_2 . A greater degradation efficiency of MNZ was observed over the entire reaction time at low TiO_2 dosage. This phenomena can be explained by the increased blockage of the incident UV light with increasing photocatalyst dosage [18,29]. Since the photocatalytic degradation of MNZ was not much increased over the 0.5 g/L of TiO_2 , further experiments were

performed with 0.5 g/L TiO_2 . Similar results have been reported by other researchers [23,24,27].

Biodegradability of MNZ was evaluated in this work. To measure the biodegradability, BOD5 and COD values were measured before and after UV irradiation and the ratio of BOD5/COD was used as a biodegradability indicator. After 3 h reaction time, removal efficiency of COD was above 97.6% at all catalyst dosages and the ratio of BOD5/COD increased from 0 to 0.098 as the dosage increased from 0.5 to 3 g/L. This result indicates that MNZ can be changed to more biodegradable products.

Effect of pH

Effect of pH on the photocatalytic degradation of MNZ (80 mg/L) was investigated at constant TiO_2 dosage (0.5 g/L) by varying the initial pH of solution. Figure 5

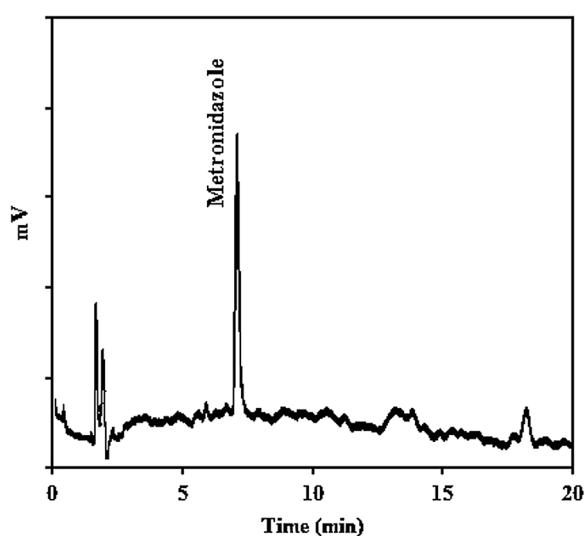


Figure 3 A typical HPLC chromatogram of Metronidazole.

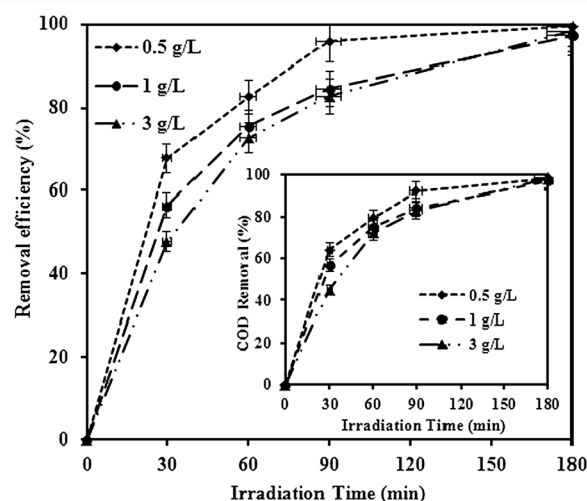
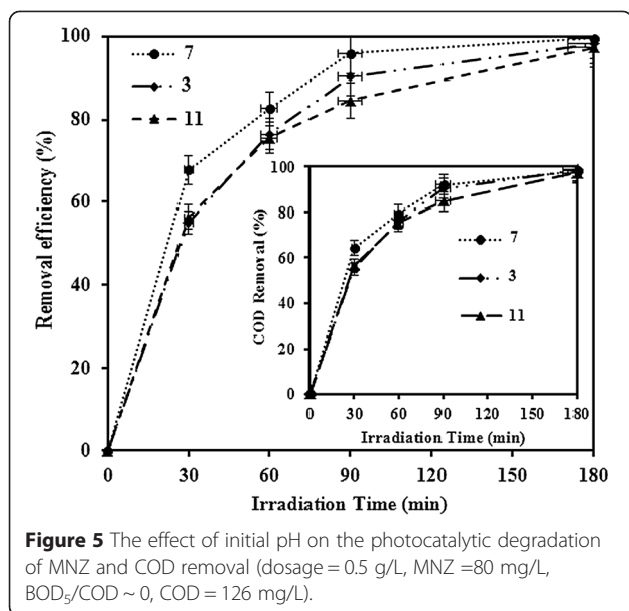


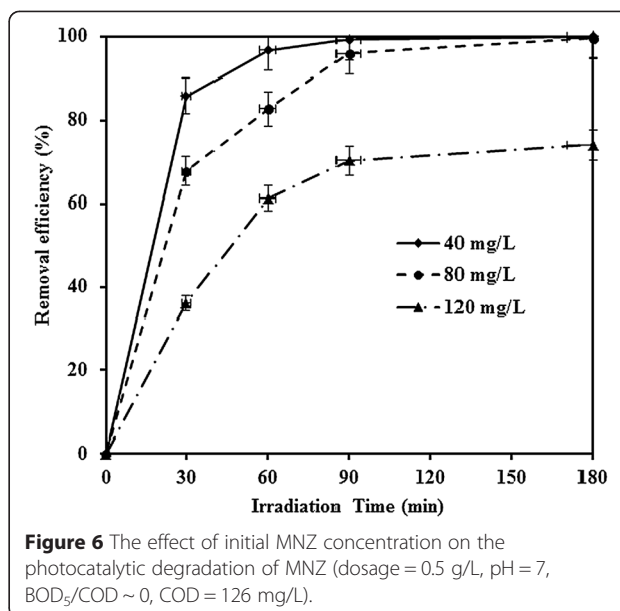
Figure 4 The effect of catalyst dosage on the photocatalytic degradation of MNZ and COD removal (pH = 7, MNZ = 80 mg/L, BOD₅/COD ~ 0, COD = 126 mg/L).



shows that the greatest degradation efficiency was obtained at neutral pH over the entire reaction time. MNZ degradation after 180 min in pH 3, 7 and 11 was 98.2, 99.48 and 97.3%, respectively. Also, COD removal after 180 min in pH 3, 7 and 11 was 97.61, 98.02 and 96.82%, respectively. This trend can be explained by the variation of charges on MNZ as well as on the surface of TiO₂ at different solution pH. The pH_{ZPC} of TiO₂ is determined as 6.52 and pK_a value of MNZ is 2.55. Therefore, at acidic pH, both TiO₂ and MNZ are positively charged, causing negative effect for the adsorption of MNZ on the surface of TiO₂. At neutral pH, no repulsive forces between the TiO₂ and MNZ might be developed. At basic pH, both TiO₂ and MNZ have negative charges, causing negative effect for the adsorption of MNZ on the surface of TiO₂. In this study, even though a distinct removal efficiency of MNZ was not observed at different solution pH, the most effective degradation of MNZ was observed at pH 7. Thus further experiments were performed at neutral pH [4,15,18].

Effect of initial MNZ concentration

Photocatalytic degradation of MNZ by TiO₂ was studied by varying the initial MNZ concentration at pH 7 and dosage equal to 0.5 g/L. Figure 6 shows that photocatalytic degradation efficiency decreased as the initial MNZ concentration increased. The presumed reason is that more surface of the TiO₂ surface may be occupied by MNZ as the initial MNZ concentration increased. In addition, more degradation intermediates can be accumulated on the TiO₂ surface, causing a negative effect in the utilization of hydroxyl radicals or positive holes in



the valence band of the TiO₂ surface. Moreover, once the concentration of the MNZ increases, more absorption of UV light by MNZ molecules, known as inner filtration effect, can occur. This effect causes decrease of photons reaching to the TiO₂ surface [4]. Similar results have been reported by other researchers [15,18,23].

Kinetic study and electrical energy determination

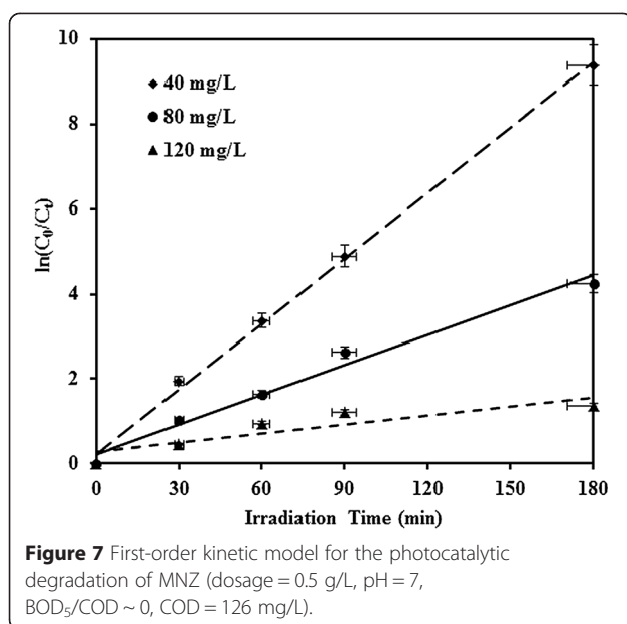
In order to obtain kinetic information, experimental result in Figure 6 was fitted with a pseudo-first-order equation as expressed in Eq. (2).

$$\ln[(\text{MNZ})_0/(\text{MNZ})_t] = k_1 t \quad (2)$$

To calculate the rate constant from the plot $\ln[C_0/C]$ versus t , only initial data points were considered. Figure 7 shows the plot of $\ln[C_0/C]$ versus t for the degradation of MNZ. The first-order rate constants of photocatalytic process (k_{obs} (1/min)) at different initial concentrations of MNZ are summarized in Table 2. The relationship between the initial photocatalytic degradation rate (r) and the initial concentration of organic substrate for a heterogeneous photocatalytic process can be described by Langmuir–Hinshelwood (L-H) model (Eqs. 3 and 4) [30,31]:

$$r = \frac{k_c K_{\text{MNZ}} [\text{MNZ}]}{1 + K_{\text{MNZ}} [\text{MNZ}]_0} = k_{\text{obs}} [\text{MNZ}] \quad (3)$$

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_c K_{\text{MNZ}}} + \frac{[\text{MNZ}]_0}{k_c} \quad (4)$$



where $[MNZ]_0$ is the initial concentration of the antibiotic in mg/L, k_c (mg/L/min) is the kinetic rate constant of surface reaction and K_{MNZ} (L/mg) is the Langmuir adsorption constant. The values of K_{MNZ} and k_c were obtained as 0.0285 L/mg and 0.67 mg/L/min, respectively. This L-H kinetic model has been used by several authors to analyze heterogeneous photocatalytic reactions [30,31].

For the case of photocatalytic reaction, electrical energy is very important factor for the real application and evaluation for the electrical energy should be provided. Thus, in this work, electrical energy was evaluated by calculating electrical energy per order (E_{EO}). It is defined as the number of kWh of electrical energy required to reduce concentration of a pollutant by 1 order of magnitude (90%) in 1 m³ of contaminated water. The E_{EO} (kWh/m³) can be calculated from the following equation:

$$E_{EO} = \frac{p \times t \times 1000}{V \times 60 \times \log(C_i/C_f)} \quad (5)$$

Table 2 Pseudo-first order kinetic parameters and E_{EO} values for the photocatalytic degradation of MNZ at different initial MNZ concentrations (catalyst dose = 0.5 g/L and pH = 7)

E_{EO} (kWh/m ³)	R^2	$1/k_{obs}$ (min)	k_{obs} (1/min)	$[MNZ]_0$ (mg/L)
93.57	0.998	19.493	0.0513	40
206.01	0.9828	42.918	0.0233	80
666.67	0.7874	138.888	0.0072	120

Table 3 The E_{EO} values for the removal of MNZ ($[MNZ]_0 = 80$ mg/L, catalyst dose = 0.5 g/L and pH = 7)

Process	E_{EO} (kWh/m ³)
UV 8 W-alone	290.11
UV125W-alone	245.17
UV 8 W/TiO ₂	230.04
UV 125 W/TiO ₂	197.95

$$E_{EO} = \frac{38.4 \times P}{V \times k_{obs}} \quad (6)$$

where P is the rated power (kW) of the AOP system, t is the irradiation time (min), k_{obs} is the pseudo-first order rate constant (1/min), V is the volume (L) of the wastewater in the reactor, C_i and C_f is the initial and final MNZ concentrations, respectively. The E_{EO} value for UV-alone and UV/TiO₂ processes are reported in Table 3. E_{EO} value for UV/TiO₂ process was lower than UV-alone process.

Comparison of different MNZ removal processes and reusability test

MNZ removal by TiO₂-alone, UV 8 W-alone, UV 125 W-alone, UV 8 W/TiO₂ and UV 125 W/TiO₂ processes are shown in Figure 8. Removal efficiency of MNZ through adsorption process (TiO₂-alone) was low. Overall removal efficiency of MNZ by TiO₂-alone, UV 8 W-alone, UV 125 W-alone and UV 8 W/TiO₂ process was 9.63%, 24.52, 42.32% and 53.53%, respectively. But 99.48% of

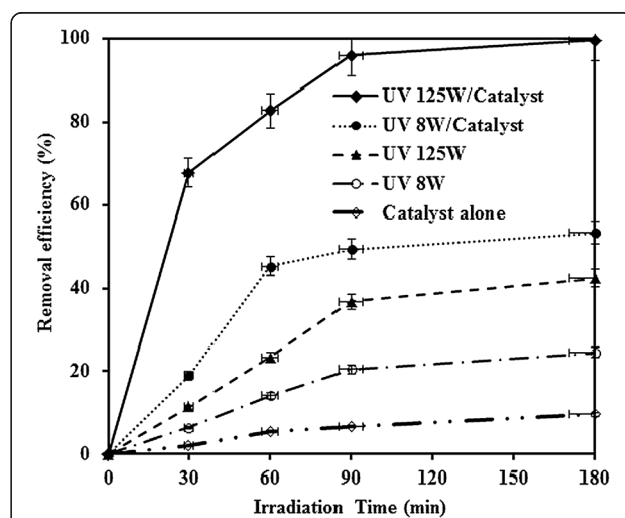
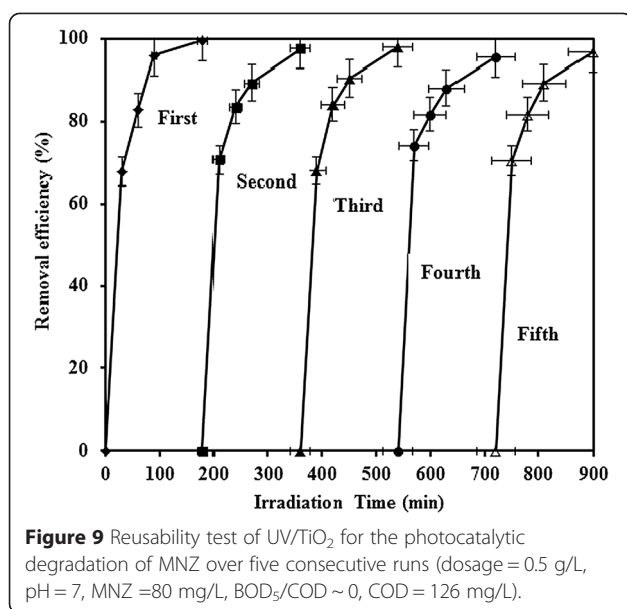


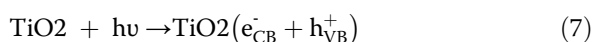
Figure 8 The contribution of each process involved in the photocatalytic degradation of MNZ (dosage = 0.5 g/L, pH = 7, MNZ = 80 mg/L, BOD₅/COD ~ 0, COD = 126 mg/L).



MNZ was removed with UV 125 W/TiO₂. These experiments demonstrate that both UV light and TiO₂ are necessary for the effective degradation of MNZ.

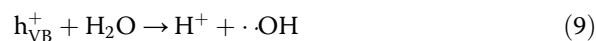
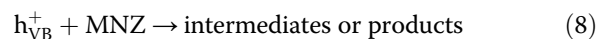
Based on the above experiments and analysis, mechanism of the photocatalysis could be proposed as following:

An electron excites from the valence band to the conduction band of TiO₂, generating electron-hole pair, with UV light ($\lambda < 390$ nm) (Eq. 7) [24,27]:



Then, the generated electron-hole pairs can participate in the reactions with electron acceptors like O₂ and donors like H₂O or OH⁻ to generate highly reactive radical species particularly hydroxyl radicals ($E^0 = +3.06$ V),

which can oxidize organic contaminants and their degradation intermediates unselectively. Furthermore, positive holes can oxidize pollutants directly, too (Eqs. 8–11) [24,27]. Also Homem and Santos [32] reviewed degradation and removal methods of antibiotics from aqueous matrices and suggested removal mechanisms.



The reusability of a photocatalyst is an important factor for real application. Hence, five consecutive photocatalytic experiments were performed by UV/TiO₂ process. As can be seen in Figure 9, quite similar photocatalytic activity was maintained over five consecutive runs. Photocatalytic degradation of MNZ with illuminated TiO₂ was compared with other reported data. Removal efficiency and reaction rate constant were compared and summarized in Table 4.

Conclusions

From the application of TiO₂ for the photocatalytic degradation of MNZ in aqueous solutions, a maximum removal of MNZ was observed at neutral pH. Removal efficiency was decreased by increasing TiO₂ dosage and initial MNZ concentration. Electrical energy per order was increased and reaction rate constant was decreased with increasing initial MNZ concentration. Photocatalytic activity was maintained even after five consecutive runs. Finally, UV/TiO₂ is identified as a promising technique for the removal of MNZ with high efficiency in a relatively short reaction time.

Table 4 Comparison of photocatalytic degradation of MNZ

Systems	pH	Catalyst dosage (g/L)	[MNZ] ₀ (mg/L)	Lamp (W)	Time (min)	Removal efficiency (%)	k _{obs} (min ⁻¹)	Reference
Visible/ZnO	-	1.0	5	300	160	16.9	-	[3]
Visible/ZnO-RGO	-	1.0	5	300	160	49.3	-	[3]
Visible	-	-	5	300	160	5.5	-	[3]
UV/ZnO	10	1.5	80	125	180	96.55	-	[4]
UV	6	-	0.006	Lp Mp	5 5	6 12	0.005616 0.02304	[16]
UV/Niobate K ₆ Nb _{10.8} O ₃₀	-	1.5	10	18	180	57	0.00449	[18]
UV/TiO ₂	7	0.5	80	125	120	99.48	0.0233	Present study

Competing interests

The authors declare that they have no competing interests.

Authors' contribution

MF carried out the degradation studies of Metronidazole. EB contributed in writing of the manuscript and analyzing of data. AE involved in design of removal experiments, analyzing of data. J-KY discussed XRD and FT-IR data of titanium dioxide and participated in the sequence alignment of the manuscript. MS-S involved in design of removal experiments, analyzing of data, writing of the manuscript and reviewing of the manuscript. All authors read and approved the final manuscript.

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Author details

¹Department of Environmental Health Engineering, School of public Health, Iran University of Medical Sciences, Tehran, Iran. ²Health Promotion Research Center, Zahedan University of Medical Sciences, Zahedan, Iran. ³Divisions of General Education, Kwangwoon University, Seoul 139-701, South Korea.

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